DECLARATION

I, Masao Katsura, do solemnly and sincerely declare that I understand the Japanese language and the English language well, and that the attached English version is a full, true and faithful translation made by me of Japanese Application for Patent No. 2004-100414. I make this solemn declaration conscientiously believing the same to be true.

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[Document Name] Claims

[Claim1]
A treating material for ammonia containing wastewater comprising agglomerate of an anaerobic autotrophic ammonia-oxidizing bacteria exist in a core and agglomerate of an aerobic autotrophic nitrifying bacteria exist on a surface and a thickness of the agglomerate of the aerobic autotrophic nitrite bacteria is not less than 5 mm in water.

[Claim2]
The treating material for ammonia containing wastewater according to claim 1, wherein the bacterial agglomerate is attached on a carrier.

[Claim3]
The treating material for ammonia containing wastewater according to claim 2, wherein the carrier is composed of a filament component like net, fabrics or a non-woven fabric,

[Claim4]
The treating material for ammonia containing wastewater according to claim 3, wherein the filament component like net is made of acrylic resin.

[Claim5]
The treating material for ammonia containing wastewater according to claim 3, wherein the non-woven fabric is made of polyester or polypropylene.

[Claim6]
The treating material for ammonia containing wastewater according to claim 2-5, wherein the carrier is fixed partially to a frame.

[Claim7]
An apparatus for ammonia containing wastewater, wherein the treating material according to claim 1-6 is provided.

[Claim8]
A process for treating ammonia containing wastewater comprising bringing ammonia containing wastewater into the apparatus where the treating material according to claim 1-6 is provided in, bubbling oxygen containing gas in the wastewater, reacts ammonia into nitrite partially, and remove residual ammonia in the wastewater continuously as nitrogen gas using autotrophic ammonia-oxidizing bacteria with nitrite as hydrogen acceptor.

[Claim9]
The process for treating ammonia containing wastewater according to claim 8, wherein a dissolved oxygen concentration is not less than 1 mg/l in the

bubbling zone of the apparatus.

[Claim10]

The process for treating ammonia containing wastewater according to claim 8-9, wherein the ammonia containing wastewater has a pH of 7.5 to 8.5 and a temperature of 30 to 40.degree. C.

[Document Name] Specification
[Name of the Invention] Ammonia treating materials, a process and an apparatus for treating ammonia containing wastewater

[Field of the Invention]
[0001]
A present invention relates to a treating material, a process and an apparatus for treating ammonia containing wastewater,

[Back ground of the Invention]
[0002]
We have been forced to change our lifestyle from the mass production, mass consumption and mass disposal one in the 20th century to the recycling and low-load way of life. The spread of wastewater treatment services improves the quality of wastewater discharged to public water areas year by year. However, closed water bodies such as lakes and inland seas often have increased concentrations of nutrient salts such as nitrogen and phosphorous. The consequent eutrophied phenomena such as red tides are social problems. Accordingly, there is a need for an advanced, efficient and economic process capable of reducing organic matters and nutrient salts such as nitrogen and phosphorous in wastewater.
[0003]
There are two general biological processes for removing nitrogen in wastewater: one is nitrogen removal by biological uptake and the other is nitrogen removal using nitrification and denitrifying. In the former process, bacteria assimilate nitrogen as they grow. However, treating wastewater over time results in accumulation of bacteria in an apparatus, causing the need of eliminating and disposing the bacteria. The bacteria disposed cause a waste problem.
[0004]
The other hand, according to a process using nitrogen cycle, $NH_4^+$is oxidized with ammonia-oxidizing bacteria such as Nitrosomona into NO_2^- and after that NO_2^- is oxidized into NO_3^- with nitrite bacteria such as Nitrobacter , and then reduces NO_3^- is reduced into nitrogen gas with denitrifying bacteria under anaerobic conditions, that is, with nitrification/denitrifying process. .
[0005]
The other hand, according to a process using nitrogen cycle, $NH_4^+$is oxidized with ammonia-oxidizing bacteria such as Nitrosomona into NO_2^- and after that NO_2^- is oxidized into NO_3^- with nitrite bacteria such as Nitrobacter , and then reduces NO_3^- is reduced into nitrogen gas with denitrifying bacteria under anaerobic conditions, that is, with nitrification/denitrifying process. .
[0006]
The typical nitrification-denitrifying processes such as nitrification-denitrifying with circulation of nitrified liquid, and A_2O process are only capable of approximately up to 80% total nitrogen removal.

Although the triplex processes are expected to enable high total nitrogen removal, the used denitrifying bacteria is heterotrophic nutrition and require external supply of carbon sources such as methanol, increasing costs. Accordingly, there is a need for the development of an economic nitrogen removal process as a replacement for the conventional nitrification-denitrifying processes.

[0007]

Recently, Graaf, et al. found anaerobic autotrophic denitrifying bacteria capable of reducing ammonia and nitrite into N_2 gas. The bacteria are utilized in an ammonia-nitrogen removing reaction called Anammox reaction, and the bacteria for Anammox reaction is called Anammox bacteria,

[0008]

Anammox reaction is a autotrophic denitrifying reaction under a anaerobic condition using NH_4^+ as an electron donor and NO_2^- as an electron acceptor. To remove nitrogen from wastewater, it is needed to nitrite ammonia as a pre-reaction. In the case, half of NH_4^+ is oxidized into NO_2^-,

[0009]

At present, there are only a few Anammox reactions in practical use. This is because 3 reasons, (1) Anammox bacteria is a autotrophic and have an extremely slow growth rate, (2) ammonia and nitrite have to form an equimolar mixture, but controlling these amounts is not easy, and (3) at least two reaction tanks, nitrite tank and denitrifying tank, are required, making the apparatus large-scale. To solve the problem, some ideas are proposed.

[0010]

Patent Document 1 discloses a process in which approximately half of ammonia in a liquid phase is oxidized into nitrite and ammonia and nitrite in the liquid phase are brought into contact with bacteria in the absence of oxygen and are converted into N_2 gas, which is removed from the system. However, oxidizing approximately half of ammonia in the liquid phase and converting it perfectly into nitrite is thought difficult. Furthermore, the reaction requires two steps, which are a nitrite step and a denitrifying step.

[0011]

Patent Document 2 discloses a treating process of nitrogen and phosphor containing wastewater that a partial denitrifying is performed with fluid from escape phosphorous step in the first denitrifying step, where presence of autotrophic nitrifying bacteria and autotrophic ammonia oxidizing bacteria coexist under a slightly aerobic condition and in the second denitrifying step; denitrifying is carried out in the presence of autotrophic denitrifying bacteria under an anaerobic condition. However, in the process, the activity of the aerobic nitrifying bacteria is limited because of lightly aerobic condition. The slightly aerobic conditions can adversely affect the growth and activity of the anaerobic autotrophic ammonia oxidizing bacteria. Consequently, the treatment loading rate is reduced.

[0012]

Patent Document 3 discloses a treating process for ammonia containing

wastewater that a first step is the step to nitrify ammonia containing fluid using nitrification microorganism under a controlled airing condition and under pH 7.2 and a second step is the step to perform the mixture of ammonia and the oxidized product into nitrogen by denitrifying microorganism. Moreover, in this document, the first step and the second step are performed at a time in a single bioreactor and coexisting autotrophic nitrifying microorganism and denitrifying microorganism in a solid phase, where autotrophic nitrifying microorganism exist essentially outside aerobic parts of the solid phase and denitrifying microorganism exist in anaerobic part of the solid phase. But a detail explanation described in the document shows only the solid state is 0.1-1mm particle carrier which suport biofilm or immobile particle carrier which support biofilm. The concrete example is not shown there. Anyway, Patent Document 3 shows that the process is performed under controlled oxygen concentration. It means that the nitrifying reaction of autotrophic nitrifying microorganism which needs oxygen cannot go smoothly. And the slightly aerobic conditions can adversely affect the growth and activity of the anaerobic denitrifying microorganism. Consequently, the treatment loading rate is reduced.

[Patent Document 1] JP-A-2001-37467
[Patent Document 2] JP-A-2003-126888
[Patent Document 3] JP-A-2001-506535

[DISCLOSURE OF THE INVENTION]
[Problems to be Solved by the Invention]
[0013]

The present invention is directed to provide a treating material, a treating apparatus, and a process for treating ammonia containing wastewater efficiently. The purpose of this invention is to provide such a process which can go both nitrite and denitrify reaction at a time in a reacting tank, therefore it is economical and energy eliminated. Another purpose of this invention is to provide such a treating material, a treating apparatus, and a process for treating ammonia containing wastewater which do not produce needless agglomerate and do not need agglomerate sintering tank. Another purpose of this invention is to provide a such economical and energy saving treating material, treating apparatus, and a process for treating ammonia containing wastewater which neither need mixing items nor motor power to circulate wastewater because of circulating wastewater with oxygen containing air. Another purpose of this invention is to provide a treating material, a treating apparatus, and a method for treating ammonia containing wastewater such a process which can go both nitrite and denitrifying at a time in a reacting vessel at high speed without limiting to provide oxygen in the wastewater.

[MEANS FOR SOLVING THE PROBLEMS]
[0014]

The present invention is that a treating material for ammonia containing wastewater comprising a agglomerate of an anaerobic autotrophic ammonia-oxidizing bacteria exist in a core and an aerobic autotrophic nitrifying bacteria exist on a surface and a thickness of the agglomerate of the aerobic autotrophic nitrite bacteria is not less than 5 mm in water.
[0015]
The bacterial agglomerate of the invention is preferably attached on a carrier. The carrier of this invention is preferably composed of a filament component like net, fabrics or a non-woven fabric. The filament component like net of this invention is preferably made of acrylic resin. The non-woven fabric is preferably made of polyester or polypropylene.
[0016]
The carrier of this invention is preferably fixed partially to a hollow frame.
[0017]
The present invention is an apparatus for ammonia containing wastewater wherein the above mentioned treating material is provided.
[0018]
Looking from another aspect, the present invention is a process for treating ammonia containing wastewater comprising bringing ammonia containing wastewater into the apparatus where the above mentioned treating material is provided in, bubbling oxygen containing gas in the wastewater, reacts ammonia into nitrite partially, and remove residual ammonia in the wastewater continuously as nitrogen gas using autotrophic ammonia-oxidizing bacteria by residual ammonia as hydrogen acceptor of nitrite.
[0019]
The dissolved oxygen concentration is preferably not less than 1 mg/l in the bubbling zone of the apparatus.
[0020]
The ammonia containing wastewater preferably has a pH of 7.5 to 8.5 and a temperature of 30 to 40.degree. C.

[EFFECTS OF THE INVENTION]
[0021]
The treating material, the apparatus and the process for treating ammonia containing wastewater according to the invention make it possible that nitrite and denitrifying reaction can take place efficiently at a time in a reacting vessel economically. Needless agglomerate is not produced in the process. A sintering vessel is not needed because agglomerate is fit and fixed to a carrier and treated water does not include agglomerate. Circulate treat water with oxygen containing air makes mixing apparatus and motor power needless. This invention is economical and energy saving epoch making one to solve many problems of treating wastewater using Anammox reaction.

[PREFERRED EMBODIMENTS OF THE INVENTION]

[0022]

The process for treating ammonia containing wastewater according to the present invention will be described in detail hereafter.

[0023]

The ammonia-treating material according to the invention includes bacteria agglomerate where autotrophic anaerobic ammonia oxidation bacteria agglomerate and autotrophic nitrite bacteria agglomerate are coexist. Also preferably, in the complex bacterial agglomerate, the autotrophic ammonia-oxidizing bacteria agglomerate are present in a core area and autotrophic nitrite bacteria agglomerate are present on a surface area. The autotrophic anaerobic ammonia oxidation bacteria agglomerate and autotrophic nitrite bacteria agglomerate need not be an agglomerate each, but are may disperse in other microorganism. The wastewater treating material according to the invention need not consist of two agglomerate, the autotrophic anaerobic ammonia oxidation bacteria agglomerate and autotrophic nitrite bacteria, but can include other bacteria or other non-creature such as nitrifying bacteria agglomerate.

[0024]

A configuration of the bacteria agglomerate in the treating material of the invention is not particularly limited. Examples of the configurations include cube, rectangles, cylindrical, ball, oval, polygonal like cylindrical and configurations including part of these shapes, and amorphous shapes. Of these, cylindrical or polygonal columns such as hexagonal columns are preferred.

[0025]

A diameter and length of the treating material is not particularly limited. However, it is preferable to make the length of the treating material high to keep high dissolved-oxygen concentration. If the diameter is too small, it is not preferable to get high dissolved-oxygen concentration of wastewater where anammox bacteria agglomerate live. Usually, the thickness of the agglomerate cannot control because the agglomerate is formed automatically by itself at the invented treating material.

[0026]

The agglomerate of nitrite bacteria preferably have a thickness of not less than 5 mm, preferably not less than 10 mm, more preferably not less than 20 mm. When the thickness of the autotrophic nitrite bacteria is not sufficient, it is not good that the autotrophic anammox bacteria may be exposed to aerobic condition and may die from the condition.

[0027]

The agglomerate according to the invention should not move in a vessel and should be attached and fixed to a carrier. For the carrier to carrier bacteria agglomerate some kinds of material can be used. But it is preferable to use net like or non woven fabrics.

[0028]

FIG. 1 shows an example of the net as a preferable one. The net shown is a

specially-knitted three-dimensional structure, and its skeleton is made of filaments. The skeleton includes strands of a high-absorption bulky polymer that are knitted in the skeleton and are uniformly dispersed. The net has a high porosity and is bulky, and therefore laminating the nets gives a desired volume. The knitted net has high contraction and expansion properties. Consequently, the net may be contracted and fitted in a carrier such as a frame, and the density of the carrier may be easily controlled. Such net shape carrier med of polyacrylic resin to be fixed is manufactured and sold by NET as a trade name: Biofix or Bio Fringe.

[0029]

Examples of the fibers and filaments for making the nets include fibers and filaments of metals, polymers, and natural fiber like coconut and palm. Polymer filaments are preferable for their high expansion properties, excellent durability, lightweight and inexpensiveness. Polymers for monofilaments for carrier include polyethylene, polypropylene, polyester filaments, polyurethane, polyamide and polyacrylic resin. Of these, polyacrylic resin is most preferable because they have highest affinity for water and permit good attachment and immobilization of the bacteria.

[0030]

A non woven fabric also can be used according to the invention. A non woven fabric may be fabricated by blowing a molten polymer through a small-diameter nozzle to disperse and fixed to form a sheet having a uniform density.

[0031]

The materials of the non-woven fabrics include polyethylene, polypropylene, polyester, polyurethane, polyamides and polyacrylic resin. They have excellent mechanical strength, chemical resistance and durability, and are lightweight and inexpensive. Of the above materials, polyester and polypropylene are more preferable for their superior forming properties and strength, and small fiber diameters.

[0032]

A preferred method for manufacturing the treating material, which includes the nitrite bacteria agglomerate and anammox bacteria agglomerate, can be shown ,for example as described hereafter as an example, by continuing nitrite at the situation that the agglomerate of nitrite bacteria is attached and immobilized on the carrier until appearing anammox bacteria agglomerate in the bacteria agglomerate.

[0033]

The following process is also preferable. Anammox bacteria sludge is dispersed in water or wastewater having a dissolved-oxygen concentration of 0 mg/l or nearly 0 mg/l where the carrier is set previously, circulated by oxygen free gas, for example N_2 gas, or mixing device, anammox bacteria agglomerate (sludge) are attached and immobilized to the carrier at first. Subsequently, water or wastewater in which nitrite bacteria sludge is dispersed is supplied while being circulated by oxygen free gas, for example

N_2 gas, or mixing device. Consequently, the nitrite bacteria are attached and immobilized on the outer surface of the anammox bacteria agglomerate.

[0034]

The net above mentioned is preferably fitted and fixed in a hollow frame having excellent shape stability and high rigidity, whereby the shape of the net is stabilized and the long carrier is easily installed in and removed. The materials of the frame include metals and polymers. Among them, polymers are preferable for their non-corrosion properties. Examples of the polymers as carriers include polyethylene, polypropylene, polyvinyl chloride, unsaturated polyester, polyamide and ABS resin.

[0035]

An example of the apparatus according to the present invention is shown in FIG. 2. FIG. 2 is a schematic figure of an apparatus according to the invention. In FIG. 2, 1 is a denitrifying apparatus, 2 is agglomerate of bacteria with fiber carrier, 3 is reaction water, 4 is an inlet of wastewater, 5 is a inlet of air, 6 is a air guide tube, 7 is a treated water outlet, 8 is a pH controller, 9 is a temperature controller and 10 is upper air phase.

[0036]

The invented reaction apparatus includes the invented treating materials. There may be one or more treating materials. The treating materials are preferably situated to surround an air inlet.

[0037]

Wastewater to be treated is supplied from a wastewater inlet. And the treated wastewater is discharged from the effluent outlet. To prevent wastewater flow out without treat, that is, to prevent short circuit of the wastewater, a partition wall (not shown) is preferably provided between the wastewater inlet and the effluent outlet to permit communication only at a bottom part in the reaction tank.

[0038]

An air inlet pipe is preferably provided in a central area, and air is forcibly blown and bubbling the wastewater to produce the wastewater flows and to provide oxygen to the wastewater in the apparatus according to the invented apparatus. It is prefer to circulate water by the blowing air.

[0039]

By above mentioned such bubbling air procedure, the dissolved oxygen concentration in the wastewater at the bubbling area is desirably not less than 1 mg/l, preferably not less than 2 mg/l, optimally not less than 5 mg/l. When the dissolved oxygen concentration is extremely low, the nitrite reaction by the nitrite bacteria is not performed smoothly, wastewater-treating ability is lowered and the nitrite bacteria is inhibited at extremely case.

[0040]

A mixing device is not needed to circulate reaction water in the present treating apparatus, but is preferable to circulate them by blowing air in the invented apparatus. It is preferable to settle an air guide pipe as is drawn in

Fig.2 above the air inlet.
[0041]
The invented apparatus should have an automatic temperature controller for keeping the wastewater temperature in the reaction tank constant.
[0042]
The invented treating apparatus should be designed such that the pH of the wastewater in the reaction tank is measured automatically or manually adjusted to a desired level. .
[0043]
The reaction in the invented apparatus is generally controlled by manipulating conditions such as supply (1) amount of the wastewater, (2) pH of the wastewater and (3) wastewater temperature in the reaction tank. Accordingly, it is preferable that the data, particularly the ammonium nitrogen concentration of wastewater supplied in the reaction tank is beforehand detected and is preferable to provide capable of automatic manipulation of the conditions to keep the nitrogen concentration in the treated wastewater below a predetermined level by changing above mentioned factors.
[0044]
A shape of the invented treat apparatus may preferably be cylindrical and long in the height direction as is used for reaction apparatus. Alternatively, a shape of the reaction tanks may be polygonal in cross section such as triangular, rectangular, pentagonal or hexagonal. A hexagonal cross section is most preferable because it is nearly circular and permits high efficiency of wastewater treatment. To achieve higher efficiency of wastewater treatment, a plurality of partition walls in a honeycomb form may be provided in the reaction tank.
[0045]
For the invented treating apparatus, the reaction tank should not be limited one, but could be in multi steps in which the wastewater is treated through a plurality of reaction tanks to obtain high treatment rate or high total nitrogen removal. A plurality of reaction tanks may be arranged parallel to enable to treat high volume of wastewater and treat continuously without interruption during repair and check of the reaction tank.
[0046]
In the invented wastewater treating process, at first, wastewater is provided to the above mentioned treat apparatus. The wastewater may be supplied continuously. The ratio of supply may be determined, depending on wastewater treatment conditions, is usually in the range of 0.1 to 1 kg NH_4-N/m^3/day. Herein, kg is the total amount of NH_4-N in the wastewater supplied, and m^3 is the volume of the reaction tank.
[0047]
A wastewater used according to the invention is not particularly limited as long as it is industrial or domestic wastewater rich in ammonium nitrogen. It is preferable to use waste which is from excreta of domestic animal and

subjected to a primary treatment such as activated agglomerate treatment to reduce organic matters inasmuch as the biological oxygen demand (BOD) is not more than 300 mg/l and the C/N ratio is low.

[0048]

The wastewater treatment according to the invention is performed under aerobic conditions, namely in the presence of oxygen dissolved in the wastewater in the reaction tank and preferably while supplying oxygen containing gas in the wastewater in the reaction tank. Air may be replaced by oxygen or an oxygen-containing gas, and air itself is preferable. As used herein, air comprehends oxygen-containing gas. Air is preferably supplied in the wastewater through a central bottom area of the reaction tank. Oxygen in air dissolves in the wastewater as bubbles rise in the reaction tank. The dissolution rate of oxygen in the wastewater is low, therefore it is preferable that the dissolved oxygen content should be increased by increasing the height of the reaction tank, supplying micro bubbles with small diameters, or using an auxiliary tank where a micro bubble generator is provided.

[0049]

In the invented treating process, a circulate flow is formed by the blowing air and there is no need to use the other force flow, for example, mixing. In the invented treating process, the wastewater in the reaction tank is preferably circulated such that an upward wastewater flow created in a central area in the reaction tank, and a downward wastewater flow produced in an inner peripheral area in the reaction tank.

[0050]

In the treating process of the invention, at first, the ammonium nitrogen in the wastewater is partially oxidized into nitrous acid by autotrophic ammonia oxidizing bacteria which exist in a surface area of the invented treating material in a aerobic condition. The reaction can be shown by Formula (1).

[0051]

[Chemical 1]

$$NH_4^{+}+1.5O_2^{-} \rightarrow NO_2^{-}+H_2O+2H^{+} \quad \cdots (1)$$

[0052]

In the treating process of the invention, subsequently, NH_4-N remaining in the wastewater and nitrous acid, which was produced by above mentioned autotrophic ammonia oxidizing bacteria, are converted into N_2 gas by autotrophic anammox bacteria in a same single reaction tank where the wastewater was oxidized into nitrous acid. This nitrogen removal reaction using anaerobic anammox bacteria is known as “an anammox reaction”. The reaction is considered to perform as the following Formula (2).

[0053]

[Chemical 2]

$$NH_4^{+}+ NO_2^{-} \rightarrow N_2+2H_2O \quad \cdots (2)$$

[0054]

In the treating process of the invention, air is preferably provided at a

bottom of the reaction tank and reaction is performed in aerobic condition. The reason is not clear why both ammonia oxidation bacteria and anammox bacteria can coexist. But the reason for this will be explain such as follows. Nitrite bacteria agglomerate covers outside of anammox bacteria agglomerate according to the invented treating materials. In the treating process of the invention, the wastewater is not mixed forcefully, but is circulate by air flow. It can be considered that reaction substrates are get into toward center of the agglomerate with dispersal power at the condition. Oxygen, which is dissolved in the wastewater, also disperses toward inner of the agglomerate. However, the dissolving speed of oxygen to the treat water and transfer speed are so slow that dissolved Oxygen is consumed by organism oxidation bacteria or ammonia oxidation bacteria which exists near surface of the agglomerate and can not reach to the anammox bacteria in the core area. That is, atmosphere around anammox bacteria is in an oxygen poor condition or anaerobic condition. Accordingly, the surface area of the agglomerate is a good circumstance for ammonia oxidization bacteria in oxygen rich atmosphere and inner area of the agglomerate is a good circumstance for anammox bacteria in oxygen free atmosphere.

[0055]

The growth rate of the anammox bacteria can be improved extremely by addition of inorganic salts to the ammonia containing wastewater or the incubate water.

[0056]

Examples of the inorganic salts to be used for the purpose include potassium chloride, sodium chloride, calcium chloride, magnesium chloride, zinc chloride, ferrous chloride, ferric chloride, potassium sulfate, sodium sulfate, calcium sulfate, magnesium sulfate, iron sulfate, EDTA and mixtures thereof. Seawater is an inexpensive source of inorganic salts to add to the treating water. The amount of the inorganic salts is preferably in the range of 0.1 to 5 g/l .

[0057]

In the invented reaction, the pH is usually adjusted to 7-9, desirably adjusted to 7.5 to 8.5. When the pH is in this range, the ammonia-oxidizing bacteria and the anammox bacteria are assumed very active for the reaction .

[0058]

The inorganic compounds, which may adjust the pH of the wastewater, include of the inorganic compounds include ammonium chloride, ammonium phosphate, potassium nitrite, potassium carbonate, potassium hydrogen carbonate, sodium nitrite, sodium carbonate and sodium hydrogen carbonate for examples. Of these, sodium hydrogen carbonate is most preferable. The inorganic compounds are preferably supplied to the reaction tank in the form of aqueous solutions.

[0059]

The treatment process of the invention uses 2 bacteria, anammox bacteria and ammonia-oxidizing bacteria, in combination. Accordingly, controlling

the reacted water temperature, that is, the reaction temperature is important for the reaction speed. The reaction temperature is usually in the range of 15 to 50.degree C., preferably 25 to 45 degree C., more preferably 30 to 40 degree. C, optimally 32 to 38 degree C..

[0060]

The mean residence time of the wastewater in the reaction tank in the invented reaction is variable depending on the configuration of the reaction tank and the load of the wastewater. Generally, it is from 30 minutes to 30 hours, preferably from 1 to 20 hours, particularly preferably from 3 to 10 hours. When the mean residence time is in the above range, most ammonia in the wastewater is converted to N_2 gas and is removed from the system.

[0061]

Phosphorous component can further be removed from the wastewater which is treated in the invented process. To remove phosphorous component, metal compound, preferably magnesium compound can be added and react with phosphorous component and ammonium residue in the wastewater, is crystallized and removed as magnesium ammonium phosphate(MAP).

[0062]

As magnesium compounds to make such MAP, magnesium chloride, magnesium carbonate, magnesium hydroxide, magnesium oxide, seawater and dromite can be listed up. It is economical to add magnesium between 1-1.2 by mole compare to phosphorous concentration in the wastewater.

[0063]

According to the treatment process of the invention, approximately 90% of ammonium nitrogen can be removed as N_2 gas, while about 5 to 10% of nitrogen components contained in the wastewater remains as nitrate nitrogen. In the treating process of the invention, the bacteria are not drastically increased as the activated agglomerate method, and the process does not require frequent withdrawal of excess agglomerate. Consequently, the apparatus can be operated continuously.

[0064]

The treated water by the invented process and with the invented apparatus, if it has not treated phosphorous component removal treatment, phosphorous acid is removed by phosphorous component removal apparatus . After that, the treated water can flow into river.

[EXAMPLES]

[0065]

The present invention will be described in detail by examples below, but it should be construed that the invention is in no way limited thereto. Measurements in Examples were carried out by methods shown in Table 1.

[0066]

[TABLE 1]

Item	Method	Remarks
pH	Portable pH meter (HACHEC 20 pH/ISE Meter)	pH in reactor was measured with NISSIN pH CONTROLLER NPH-690D
ORP	Platinum electrode method	UK-2030 manufactured by CENTRAL KAGAKU Corp Portable ORP meter
NH_4-N	OPP method Indophenol method (JIS K0102)	V-1100 Hitachi ratio beam spectrophotometer
NO_2-N	Ion chromatography(TOA ION ANALYZER IA-100) Colorimetric Method	ION ANALYZER LA-100 manufactured by Toa Denpa Kogyo Co., Ltd. Spectrophotometer used for NH_4—N
NO_3-N	Ion chromatography Ultraviolet spectrophotometric screening	ION ANALYZER LA-100 manufactured by Toa Denpa Kogyo Co., Ltd. Spectrophotometer used for NH_4—N
Alkalinity	Total alkalinity	Sewage testing method
DO conc.	Membrane electrode method	HORIBA OM-51DO

[0067]
(Example 1)
(Carrier)
As a carrier of bacteria agglomerate, a net composed of polyacrylic filaments as shown in FIG. 1 was purchased and was used. Properties of the net were shown in Table 2.
[0068]
[TABLE 2]
Properties of carrier of polyacrylic filaments

Acrylic bulky filaments	
Yarn	2/10
Length	23324 m/m^3
Diameter	2 mm
Surface area	146.5 m^2/m^3

[0069]
(Experimental Apparatus)
An apparatus as illustrated in FIG. 1 was used. The apparatus for denitrifying included a tank that was made of an acrylic resin and was 450 mm in height, 150 mm in width, 115 mm in length and 5.43 l in reaction part volume. The net, the wide 100 mm in diameter and 330 mm in height,

was attached and fixed to a frame of 110 mm in length, 110 mm in width, and 330 mm in height. The four frames were provided on each side of the apparatus.

[0070]

(Bacteria)

Nitrite sludge used in this experiment, which present inventors cultivated by fill and draw method with synthetic sewage in a laboratory, was used as a MLSS concentration of approximately 3000 mg/l. The composition of influent water medium used in the acclimatization of nitrifying activated agglomerate and in the continuous nitrite test was shown at the Table 3.

[0071]

[TABLE 3]

The composition used in the acclimatization of nitrifying activated agglomerate and in the continuous nitrite test

Component	Concentration
$(NH_4)_2SO_4$	10 to 100
KH_2PO_4	mg-N/l
$C_6H_{12}O_6$	13.6 mg/l
	20 mg-C/l

[0072]

(Experimental Method / Result)

First of all, an operation was performed to hold bacteria agglomerate to a carrier. 15g nitrifying activated agglomerate is added to 5l water and was supplied to the reaction tank. Air was continuously supplied at 1.7 mg-O_2/l from the bottom center of the reaction tank. The pH in the reaction tank was controlled with a pH controller (NPH-690D), and the water temperature in the reaction tank was controlled with a thermostat. The pH was adjusted by automatic addition of a 0.5 mol/l $NaHCO_3$ solution. After the nitrifying bacteria activated agglomerate was added, the mixture was circulated by air bubbling. The nitrifying activated agglomerate was substantially attached and immobilized on the net in about 4 hours (Fig.3).

[Example 2]

[0073]

(Continuous Treating Test)

The activated agglomerate, whichwas obtained by above method, was acclimatized for 100 days, while the influent NH_4-N concentration was gradually increased from 20 mg/l to 100 mg/l, and the mean residence time was gradually decreased from 12 hours to 6 hours. Using the activated agglomerate, continuous nitrite test was performed. Optimum conditions were found to be a pH of 7.5, a water temperature in reaction tank of 35.degree C., and a mean residence time of 6 hours. Then, 40 days continuous treating test was performed using the ammonia-treating material, at a pH of 7.5 and a water temperature in reaction tank of 35.degree C., and with a mean residence time of 5 hours. An inorganic salt

medium shown in Table 4 was added on the 25th day from the initiation of the continuous treating test.

[0074]

[Table 4]

A recipe of inorganic salt medium added.

COMPONENT	CONCENTRATION
KCl	1400mg/l
NaCl	1000mg/l
$CaCl_2$	1900mg/l
$MgSO_4 \cdot 7H_2O$	2000mg/l

[0075]

(Result)

FIG. 4 shows concentrations of NH_4-N, NO_2-N and NO_3-N in wastewater effluent during the continuous treatment, and FIG. 5 shows nitrogen consumption (%). After the addition of inorganic salt medium on the 25th day since the experiment starts, the NH_4-N and NO_2-N concentrations reduced, and the nitrogen removal increased, indicating the progress of the anammox reaction.

[Example3]

[0076]

More 150 days continuous treating test was performed NH_4-N content in wastewater influent was changed from 100 mg/l to 125 mg/l. FIG. 6 shows concentrations of NH_4-N, NO_2-N and NO_3-N in wastewater effluent. FIG. 7 shows nitrogen removal ratio (%), and FIG. 8 shows NH_4-N removal ratio(%). FIG. 9 shows DO concentrations in treated water, and FIG. 9 shows pH of wastewater influent and wastewater effluent. The maximum nitrogen removal ratio was 82% at the nitrogen volume load 0.48kg/m^3/day. Immediately after initiation of the continuous treatment, the influent pH was approximately 7.25, and effluent pH was approximately 7.7. After that, the effluent pH increased to approximately 8.0 despite pH control in the reaction tank as the anammox reaction was in progress.

[Example 4]

[0077]

Bacteria in the reacting tank were stained by the FISH (fluorescence in situ hybridization) method, and a photomicrograph was taken. The result was shown as Fig. 10 -12. The anammox bacteria were stained red, and the ammonia-oxidizing bacteria were stained green. Fig,10-12 are conforcal laser scanning microphotographs of the immonia-treating material. The photographs shows that anammox bacteria and ammonia oxidation bacteria are co-exist and live separately.

[Example5]

[0078]

(Identification of Anammox Bacteria)
Bacteria in the reacting tank were collected from the middle layer of the reacting tank were analyzed for its belonging. Concretely, DNA of the bacteria collected was amplified by PCR method, and the homology was examined in the internet website of National Center for Biotechnology Information (NCBI), resulting in 100% and 88% homologies with anammox bacteria KSU-1 (AB057453.1) previously found by the present inventors.

[Possibility Use on Industry]
[0079]
The invented wastewater treating material, treating apparatus and treating process can be used for wastewater treating of high nitrogen concentration wastewater or low C/N ratio wastewater, for example, filtered water of biomass plant, filtered water of sludge, second treated water of excreta, wastewater of domestic animals, garbage ooze water or waste fluid of denitrifying drain from factories or dynamo plant.

[BRIEF DESCRIPTION OF THE DRAWINGS]
[0080]
[FIG.1] FIG. 1 is a picture showing a net made of polyacrylate used in Examples of the invention;

[FIG. 2] FIG.2 is a schematic view showing a reaction apparatus used in Examples of the invention;

[FIG. 3] FIG.3 is a picture showing bacteria growth situation in a reaction tank in Examples of the invention;

[FIG. 4] FIG.4 is a graph of concentrations of nitrogen in various forms in wastewater effluent during continuous treatment in Examples of the invention;

[FIG. 5] FIG.5 is a graph showing nitrogen removal ratio in wastewater effluent during continuous treatment in Examples of the invention;

[FIG. 6] FIG.6 is a graph of concentrations of nitrogen in various forms in wastewater effluent during continuous treatment in Examples of the invention;

[FIG. 7] FIG.7 is a graph showing nitrogen removal ratio in wastewater effluent during continuous treatment in Examples of the invention;

[FIG. 8] FIG.8 is a graph showing NH_4-N removal ratio in wastewater effluent during continuous treatment in Examples of the invention;

[FIG. 9] FIG.9 is a graph showing concentrations of DO(dissolved oxygen content) in wastewater during continuous treatment in Examples of the invention;

[FIG. 10] FIG.10 is a graph showing pH of wastewater during continuous treatment in Examples of the invention;

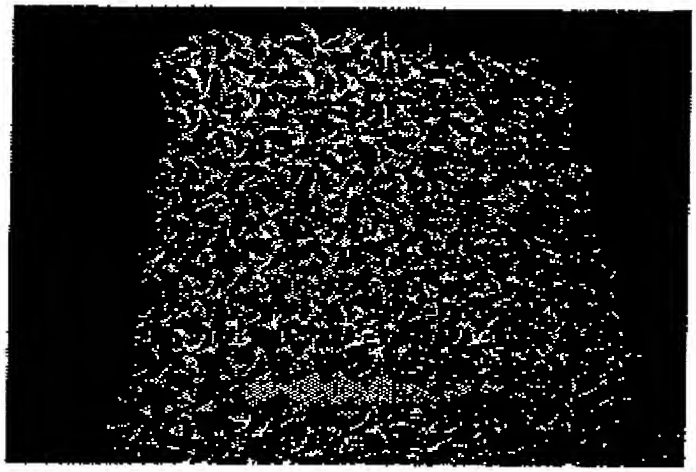
[FIG. 11] FIG.11 is a photomicrograph of bacteria agglomerate that grew in the reaction tank in Examples of the invention;

[FIG. 12] FIG,12 is a microphotograph of bacteria agglomerate that grew in the reaction tank in Examples of the invention;

[FIG. 13] FIG.13 is a microphotograph of bacteria agglomerate that grew in the reaction tank in Examples of the invention;

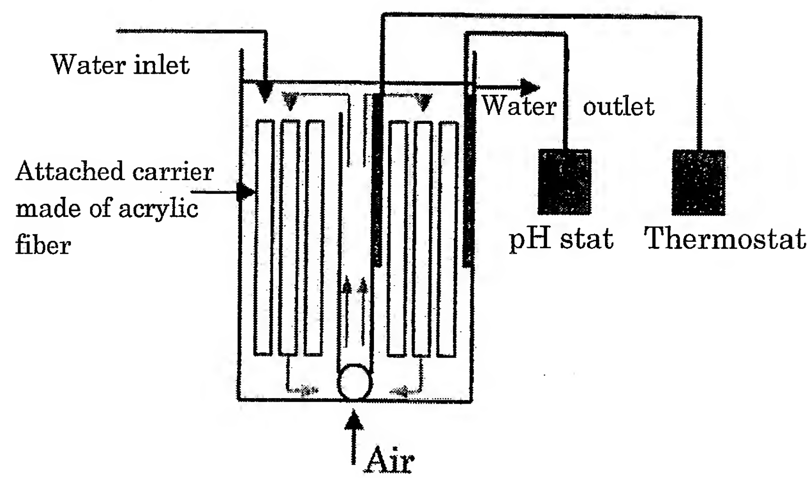
[Document Name] Drawing

[FIG. 1]



Biofix (BL)

[FIG. 2]

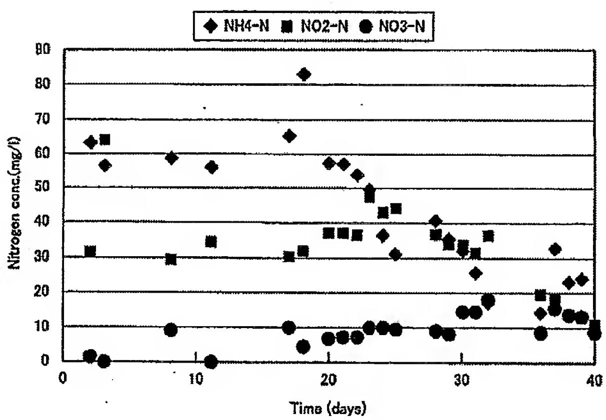


Schematic view of experiment apparatus

[FIG. 3]

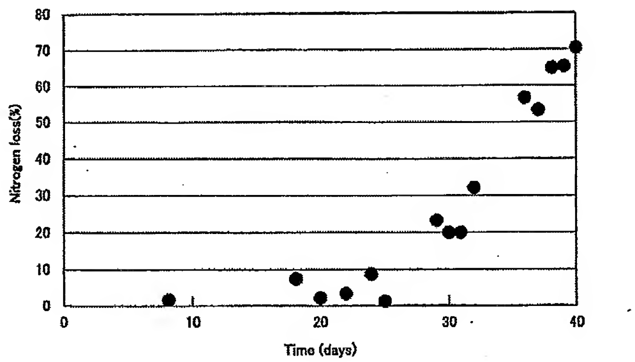
Biofilm in reaction tank

[FIG. 4]



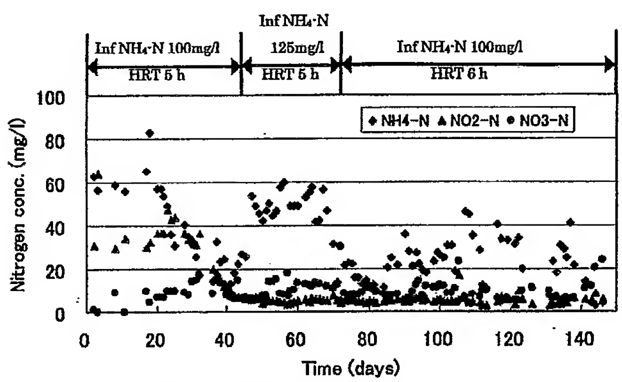
Concentrations of nitrogen in various forms in wastewater effluent during continuous treatment
Inf NH_4-N concentration 100mg/l, HRT=5h

[FIG. 5]



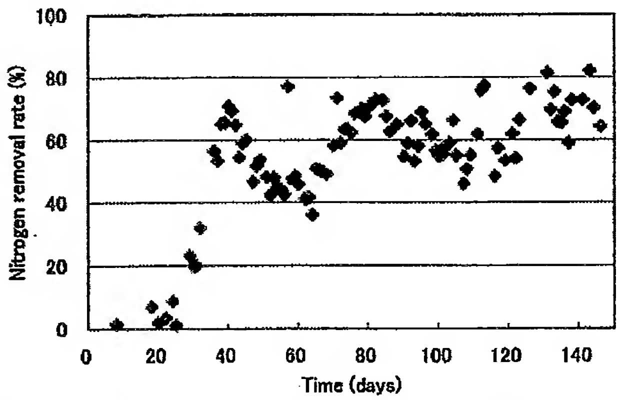
Nitrogen loss during continuous treatment

[FIG. 6]



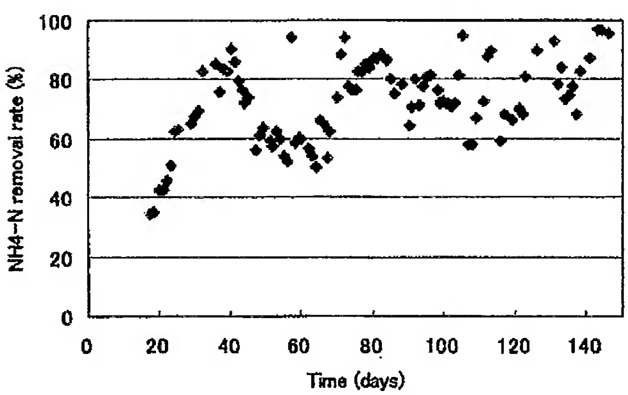
Concentrations of nitrogen in various forms in wastewater effluent during continuous partial nitritation/Anammox treatment

[FIG. 7]



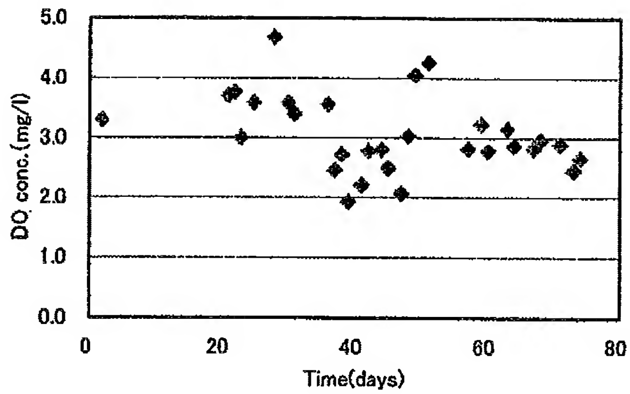
Nitrogen removal rate (%) during continuous partial nitritation/Anammox treatment

[FIG. 8]



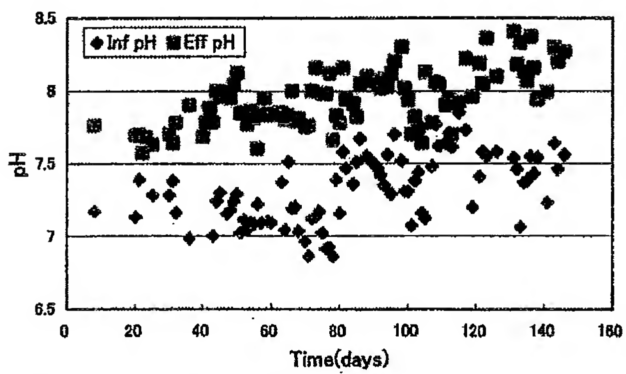
NH_4-N removal rate (%) during continuous partial nitritation/Anammox treatment

[FIG. 9]



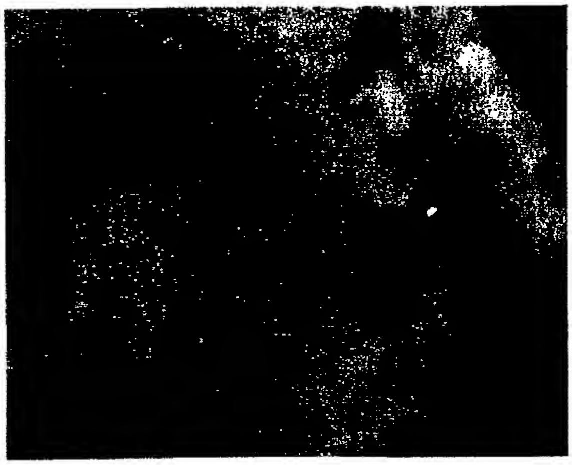
Variation per day of DO concentration

[FIG. 10]



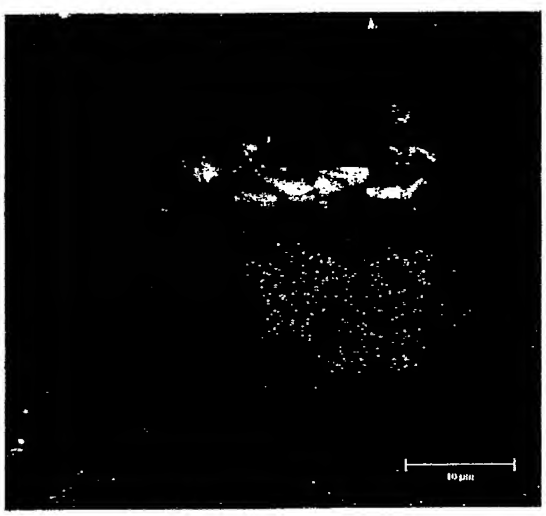
Variation per day of pH in influent water and effluent water

[FIG. 11]



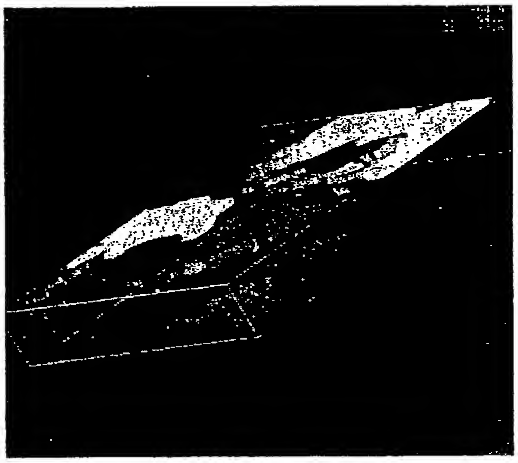
Photomicrograph by FISH method

[FIG. 12]



Conforcal laser scanning microphotograph (with scale bar)

[FIG. 13]



Conforcal laser scanning microphotograph

[Document Name] Abstract
[ABSTRACT]
[Problem]
The purpose of this invention is to provide such an ammonia containing wastewater treating material, treating apparatus and process using them which can go both nitrite and denitrify reaction at a time in a reacting tank, therefore it is economical and energy eliminated.
[Method to Solve]
A treating material for ammonia containing wastewater comprising a agglomerate of an anaerobic autotrophic ammonia-oxidizing bacteria exist in a core and an aerobic autotrophic nitrifying bacteria exist on a surface and a thickness of the agglomerate of the aerobic autotrophic nitrite bacteria is not less than 5 mm in water.
[Selected Drawing]Fig. 2